5.1. Introduction

Copper is one of the most abundant (25th in order of abundance) elements in the earth’s crust. It exists in two oxidation states, copper(I) and copper(II). The most common oxidation state of copper is +2 and copper(II) complexes have been extensively studied. These complexes have tetrahedral, octahedral, square planar and trigonal bipyramidal geometries [1]. The role of copper in organic reactions is related to its oxidation states. This metal is used in the electrical industry due to high conductivity and it is also used for water pipes because of its inertness. Copper catalyses redox reactions in biological systems primarily in the reduction of oxygen to water [2]. Due to the presence of unpaired electron, all the copper(II) complexes are paramagnetic.

Considerable interest in Schiff base compounds containing thiosemicarbazones and their transition metal complexes has grown in the areas of biology and chemistry due to biological activities [3-5]. But semicarbazone analogs received much less attention. However, semicarbazones are also reported to possess versatile structural features [6]. Their metal complexes, especially...
those containing copper(II) and iron(II) are more active than uncoordinated semicarbazones and this enhanced biological activity of metal semicarbazones has been under investigation for some time [7]. Copper(II) complexes are interesting due to their biological roles and medicinal properties.

This chapter deals with the synthesis and characterization of mononuclear and binuclear copper(II) complexes with potential NNO donor ligands, di-2-pyridyl ketone-\(N^4\)-phenyl-3-semicarbazone (HL1) and quinoline-2-carboxaldehyde-\(N^4\)-phenyl-3-semicarbazone (HL2).

5.2. Experimental
5.2.1. Materials

The semicarbazones were synthesized as discussed in Chapter 2. Solvents used were ethanol, methanol and water. Copper(II) acetate monohydrate, copper(II) sulfate pentahydrate, copper(II) nitrate hemipentahydrate, copper(II) chloride dihydrate, sodium azide and potassium thiocyanate (all are BDH, AR grade) were used as received.

5.2.2. Synthesis of complexes

\[\text{[Cu}_3\text{L}_2\text{Cl}_4\text{]} \cdot 4\text{H}_2\text{O (15)}\]

A solution of semicarbazone, HL1 (0.317 g, 1 mmol) in 20 ml of methanol was treated with a methanolic solution of the copper(II) chloride dihydrate (0.170 g, 1 mmol). The solution was heated under reflux for 4 h. The complex formed was filtered, washed with ether and dried over P4O10 in vacuo.

Yield ~0.48 g

\[\text{[CuL}_1\text{OAc (16)}\]

This complex was synthesized by refluxing methanolic solution of HL1 (0.317 g, 1 mmol) and solution of copper(II) acetate monohydrate (0.199 g, 1 mmol) in methanol for 4 h. The complex formed was filtered, washed with ether and dried over P4O10 in vacuo.

Yield ~0.50 g.
[CuL₁NO₃]₂ (17)

This complex was synthesized by refluxing methanolic solution of HL₁ (0.317 g, 1 mmol) and copper(II) nitrate hemipentahydrate (0.120 g, 0.5 mmol). The complex formed was collected, washed with ether and dried over P₄O₁₀ in vacuo.

Yield ~0.39 g.

[CuL₁N₃] (18)

A solution of HL₁ (0.158 g, 0.5 mmol) in 20 ml of methanol was treated with a methanolic solution of copper(II) acetate monohydrate (0.099 g, 0.5 mmol). The solution was heated under reflux for 1 h and sodium azide (0.032 g, 0.5 mmol) was added in portions to the solution and further refluxed for 2 h. The resulting solution was allowed to stand at room temperature and after slow evaporation complex was separated out, which was collected, washed with ether and dried over P₄O₁₀ in vacuo.

Yield ~0.55 g.

[CuL₁SCN]·3/2H₂O (19)

For the synthesis of this complex, methanolic solutions of HL₁ (0.158 g, 0.5 mmol) and copper(II) acetate monohydrate (0.099 g, 0.5 mmol) were refluxed for 1 h and methanolic solution of KCNS (0.048 g, 0.5 mmol) was added and further refluxed for 3 h. The resulting solution was allowed to stand at room temperature and after slow evaporation complex was separated out, which was collected, washed with ether and dried over P₄O₁₀ in vacuo.

Yield ~0.48 g.

[Cu(HL₁)L₁]₂(ClO₄)₂·6H₂O (20)

A solution of HL₁ (0.317 g, 1 mmol) in 20 ml of methanol was treated with a methanolic solution of the copper(II) perchlorate hexahydrate (0.185 g, 0.5 mmol).
The solution was stirred for 2 h. The complex formed was filtered, washed with ether and dried over P₄O₁₀ in vacuo.
Yield ~0.52 g.

[\text{Cu(HL}^2\text{)}\text{Cl}_2\text{]·H}_2\text{O (21)}

An aqueous solution of the copper(II) chloride dihydrate (0.170 g, 1 mmol) is mixed with a solution of the semicarbazone, HL\(^2\) (0.290 g, 1 mmol) in DMF. The resulting solution was refluxed for 5 h. The complex formed was filtered, washed with ether and dried over P₄O₁₀ in vacuo.
Yield ~0.39 g.

[\text{CuL}^2\text{OAc}·\frac{6}{5}\text{H}_2\text{O (22)}]

This complex was synthesized by refluxing a solution of HL\(^2\) (0.290 g, 1 mmol) in DMF and solution of copper(II) acetate monohydrate (0.199 g, 1 mmol) in methanol for 5 h. The complex formed was filtered, washed with ether and dried over P₄O₁₀ in vacuo.
Yield ~0.35 g.

[\text{CuL}^2\text{N}_3\text{]·CH}_3\text{OH (23)}

A solution of HL\(^2\) (0.145 g, 0.5 mmol) in 20 ml of DMF was treated with a methanolic solution of copper(II) acetate monohydrate (0.099 g, 0.5 mmol). The solution was heated under reflux for 2 h and sodium azide (0.032 g, 0.5 mmol) was added in portions to the solution and further refluxed for 2 h. The resulting solution was allowed to stand at room temperature and after slow evaporation complex was separated out, which was collected, washed with ether and dried over P₄O₁₀ in vacuo.
Yield ~0.51 g.

5.2.3. Analytical methods

The carbon, hydrogen and nitrogen analyses were carried out using a Vario EL III CHNS analyzer at SAIF, Kochi, India. Infrared spectra were recorded on a
JASCO FT-IR-5300 Spectrometer in the range 4000-400 cm\(^{-1}\) using KBr pellets. Electronic spectra were recorded on a Cary 5000, version 1.09 UV-VIS-NIR Spectrophotometer using solutions in DMSO. Magnetic susceptibility measurements were carried out on a Vibrating Sample Magnetometer using Hg[Co(SCN)\(_4\)] as a calibrant. EPR spectra were recorded on a Varian E-112 X-band EPR Spectrometer using TCNE as a standard at SAIF, IIT, Bombay, India. Molar conductivity measurements were made in DMSO solutions.

5.3. Results and discussion

The semicarbazones HL\(^1\) and HL\(^2\) were synthesized by the direct condensation of \(N^4\)-phenylsemicarbazide with di-2-pyridyl ketone and quinoline-2-carboxaldehyde respectively. These semicarbazones can coordinate with metal ions in keto and enol forms.

The complexes, \([CuL^1NO_3]_2\) (17) and \([Cu(HL^1)L^1]_2(ClO_4)_2\cdot6H_2O\) (20) were formed by the reaction of the semicarbazone, HL\(^1\) with appropriate copper(II) salt in the molar ratio 2:1. The complexes \([Cu_3L^2Cl_4]4H_2O\) (15), \([CuL^1OAc]\) (16), \([Cu(HL^2)Cl_2]_2\ H_2O\) (21) and \([CuL^2OAc]^{6/5}H_2O\) (22) were formed by the reaction of the semicarbazones with copper(II) salts in 1:1 molar ratio. In complexes \([CuL^1N_3]\) (18), \([CuL^2N_3]\cdotCH_3OH\) (23) and \([CuL^1SCN]^{3/2}H_2O\) (19), acetate anion was metathetically displaced by azide or thiocyanate anion. In the complex 21, the semicarbazone HL\(^2\) is coordinated as neutral keto form whereas in complex 20, one of the molecules of the semicarbazone, HL\(^1\) coordinates in keto form and second molecule of semicarbazone undergoes deprotonation. In all other complexes semicarbazones are coordinated in deprotonated enolate form. Complexes 15, 19, 20, 21 and 22 contain uncoordinated water molecules. Complexes 16 and 18 have general formula MLX where X is OAc and N\(_3\) respectively. The stoichiometry we assigned for all copper(II) complexes are in good agreement with CHN analyses data. For compound 15, a structure with
bridged chlorine atoms is proposed and in this compound third copper atom undergoes covalent bonding with pyridyl nitrogen atoms. The proposed structure of compound 15 is shown in the Figure 5.1.

![Proposed structure of compound 15](image)

**Figure 5.1.** Proposed structure of compound 15 (water molecules are omitted).

Magnetic moments of the complexes were calculated from magnetic susceptibility measurements. Present mononuclear copper(II) complexes exhibit magnetic moments in the range 1.51-2.04 B.M., which are close to their spin-only value. Magnetic moments of binuclear copper(II) complexes 17, 20 and 21 are at 1.40, 1.12 and 1.28 B.M. respectively [8]. Low values of magnetic moments for the binuclear complexes suggest the presence of strong antiferromagnetic spin-spin interactions. The conductivity measurements were carried out in DMSO solutions and all the complexes except 15 and 20 were found to be non-electrolytes [9]. Higher conductivity for the complex 15 may be due to the partial ionization of the complex in DMF solution. Attempts to isolate single crystals suitable for X-ray diffraction studies were unsuccessful. The analytical data of the complexes are presented in Table 5.1.
Table 5.1. Colors, elemental analyses, magnetic susceptibilities and molar conductivities of copper(II) complexes of HL¹ and HL²

<table>
<thead>
<tr>
<th>Compound</th>
<th>Color</th>
<th>Found (Calculated) %</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>μ (B.M.)</th>
<th>$\Lambda_m$²</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL¹</td>
<td>Colorless</td>
<td>67.44 (68.13)</td>
<td>4.80 (4.76)</td>
<td>22.14 (22.07)</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>[Cu₃L²Cl₂]⋅4H₂O (15)</td>
<td>Green</td>
<td>41.38 (41.69)</td>
<td>3.51 (3.50)</td>
<td>13.46 (13.50)</td>
<td>1.36</td>
<td>91</td>
<td></td>
</tr>
<tr>
<td>[CuL¹OAc] (16)</td>
<td>Brown</td>
<td>54.48 (54.73)</td>
<td>3.61 (3.90)</td>
<td>15.82 (15.96)</td>
<td>1.76</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>[CuL¹NO₃] (17)</td>
<td>Green</td>
<td>49.86 (49.92)</td>
<td>3.60 (3.19)</td>
<td>19.71 (19.02)</td>
<td>1.40</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>[CuL¹N₂] (18)</td>
<td>Green</td>
<td>51.40 (51.24)</td>
<td>3.10 (3.34)</td>
<td>26.10 (26.56)</td>
<td>2.04</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>[CuL¹SCN]²⁻⋅2H₂O (19)</td>
<td>Brown</td>
<td>48.43 (49.08)</td>
<td>3.11 (3.69)</td>
<td>18.47 (18.07)</td>
<td>2.01</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>[Cu(HL¹)L¹ClO₄]⋅2H₂O (20)</td>
<td>Green</td>
<td>50.10 (50.83)</td>
<td>3.7 (4.15)</td>
<td>16.3 (16.46)</td>
<td>1.52</td>
<td>91</td>
<td></td>
</tr>
<tr>
<td>HL²</td>
<td>Colorless</td>
<td>70.13 (70.33)</td>
<td>4.99 (4.86)</td>
<td>19.22 (19.30)</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>[Cu(HL²)Cl₂]⋅3H₂O (21)</td>
<td>Brown</td>
<td>46.87 (47.07)</td>
<td>3.30 (3.49)</td>
<td>12.71 (12.92)</td>
<td>1.28</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>[CuL²OAc]⋅6H₂O (22)</td>
<td>Brown</td>
<td>51.98 (52.64)</td>
<td>3.90 (4.28)</td>
<td>13.59 (12.92)</td>
<td>1.64</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>[CuL²N₂]FCH₂OH (23)</td>
<td>Green</td>
<td>50.13 (50.64)</td>
<td>3.42 (4.01)</td>
<td>22.15 (22.97)</td>
<td>1.51</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

a = ohm⁻¹ cm² mol⁻¹
5.3.1. Infrared spectra

The IR spectra of compounds were recorded with KBr discs in the range 4000-400 cm\(^{-1}\). The characteristic IR bands of the complexes differ from their semicarbazones, HL\(^1\) and HL\(^2\) and provide significant indications regarding the coordination and bonding sites of semicarbazones. The significant IR bands with the tentative assignments of the copper(II) complexes are presented in Table 5.2.

The presence of a strong band at 1718 cm\(^{-1}\) for the semicarbazone, HL\(^1\) is assigned to C=O stretching vibration, which is absent in complexes 15-19. This indicates that in these complexes, HL\(^1\) has undergone deprotonation and coordinated in enolate form. But in complex 20, a band at 1679 cm\(^{-1}\) is assigned as \(\nu(C=O)\) which has undergone a shift and coordination is through keto oxygen atom [10]. The coordination through keto/enol oxygen atom is further corroborated with the appearance of a band at 413-456 cm\(^{-1}\) region due to \(\nu(Cu-O)\) stretch in the spectra of the complexes [11-13]. The \(\nu_a(NH)\) vibrations of the imino group is observed at 3369 cm\(^{-1}\) in the IR spectrum of HL\(^1\) and this band disappears in the spectra of the complexes except 20, providing a strong evidence for the ligand coordination around copper(II) ion in the deprotonated form [14]. The intense band at 1591 cm\(^{-1}\) in the spectrum of HL\(^1\) has been assigned to \(\nu(C=N)\) of the semicarbazone moiety. This band is shifted to lower wavenumbers by 23-35 cm\(^{-1}\) in the spectra of complexes indicating coordination via the azomethine nitrogen [15,16]. Coordination of azomethine nitrogen is consistent with the presence of a band at ca. 504-511 cm\(^{-1}\), assignable to \(\nu(Cu-N_{azo})\) for these complexes [17,18]. But with loss of proton from N, another strong band is found in the region 1599-1597 cm\(^{-1}\) which may be due to the newly formed C=N bond as a result of enolization of the semicarbazone in complexes 15-20, again confirms the coordination via enolate oxygen. The increase in \(\nu(N-N)\) in the spectra of complexes in the
range 1143-1154 cm\(^{-1}\) is due to enhanced double bond character through chelation, thus offsetting the loss of electron density via donation to the metal ion, and is supportive of azomethine coordination. Coordination of the pyridyl nitrogen causes the out-of-plane bending vibrational band to shift from 601 cm\(^{-1}\) to higher frequencies 625, 615, 634, 621, 621 and 690 cm\(^{-1}\) respectively for the complexes 15-20 [19].

The asymmetric and symmetric stretching vibrations of the acetate group appear at 1520 and 1384 cm\(^{-1}\) respectively for the acetato complex 16 [20,21]. For the nitrato complex 17 three strong bands at 1542, 1384 and 1298 cm\(^{-1}\) are observed corresponding to \(v_1\), \(v_2\) and \(v_4\) of the nitrato group indicating the presence of a terminal monodentate coordination of the nitrato group [22]. A combination of \((v_1,v_2)\) considered as diagnostic for the monocoordinate nitrato group, has been observed at 1698 cm\(^{-1}\) [23]. \(v_3\), \(v_5\) and \(v_6\) couldn’t be assigned due to the richness of the spectrum of the complex. The azido complex 18 shows a single strong band at 2054 cm\(^{-1}\) due to the asymmetric stretching mode and the band associated with symmetric stretching mode is located at 1387 cm\(^{-1}\). Thiocyanato complex 19 has a very strong band at 2091 cm\(^{-1}\), a medium band at 775 cm\(^{-1}\) and a weak band at 493 cm\(^{-1}\) corresponding to \(v(CN)\), \(v(CS)\) and \(\delta(NCS)\) respectively [24]. The intensity and band position indicates the unidentate coordination of the thiocyanate through nitrogen atom. Perchlorate anion coordinates to the metal only when its complexes are prepared in non-aqueous solvents. The perchlorato complex 20 shows a broad band at 1097 cm\(^{-1}\) corresponding to \(v_3(ClO_4)\) and an unsplit strong band at 621 cm\(^{-1}\) assignable to \(v_4(ClO_4)\) [25]. This along with the absence of a band corresponding to \(v_1\) at 920 cm\(^{-1}\), indicates the presence of an ionic perchlorate group [26]. IR spectra of complexes 15-20 are presented in Figures 5.2-5.7.
### Table 5.2. Infrared spectral assignments (cm\(^{-1}\)) of semicarbazones and copper(II) complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu(\text{NH}))</th>
<th>(\nu(\text{C=N}))</th>
<th>(\nu(\text{CO}))</th>
<th>(\nu(\text{C=N})^a)</th>
<th>(\nu(\text{N=N}))</th>
<th>(\nu(\text{Cu–N(az)})</th>
<th>(\nu(\text{Cu–O}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL(^1)</td>
<td>3369</td>
<td>1591</td>
<td>1718</td>
<td>-</td>
<td>1129</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>([\text{Cu}_3\text{L}_2\text{Cl}_4]\cdot4\text{H}_2\text{O}(15))</td>
<td>-</td>
<td>1568</td>
<td>-</td>
<td>1599</td>
<td>1154</td>
<td>504</td>
<td>447</td>
</tr>
<tr>
<td>([\text{CuL}^1\text{OAc}]\ (16))</td>
<td>-</td>
<td>1562</td>
<td>-</td>
<td>1598</td>
<td>1146</td>
<td>507</td>
<td>413</td>
</tr>
<tr>
<td>([\text{CuL}^1\text{NO}_3]_2\ (17))</td>
<td>-</td>
<td>1568</td>
<td>-</td>
<td>1597</td>
<td>1147</td>
<td>508</td>
<td>456</td>
</tr>
<tr>
<td>([\text{CuL}^1\text{N}_3\ j]\ (18))</td>
<td>-</td>
<td>1562</td>
<td>-</td>
<td>1599</td>
<td>1144</td>
<td>504</td>
<td>414</td>
</tr>
<tr>
<td>([\text{CuL}^1\text{SCN}]^{3/2}\text{H}_2\text{O} \ (19))</td>
<td>-</td>
<td>1556</td>
<td>-</td>
<td>1598</td>
<td>1143</td>
<td>511</td>
<td>413</td>
</tr>
<tr>
<td>([\text{Cu(HL}^1\text{)}\text{L}^1\text{]}_2\text{ClO}_4\cdot6\text{H}_2\text{O} \ (20))</td>
<td>3359</td>
<td>1562</td>
<td>1679</td>
<td>1599</td>
<td>1154</td>
<td>504</td>
<td>414</td>
</tr>
<tr>
<td>HL(^2)</td>
<td>3380</td>
<td>1592</td>
<td>1702</td>
<td>-</td>
<td>1150</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>([\text{Cu(HL}^2\text{)}\text{Cl}_2\cdot6\text{H}_2\text{O} \ (21))</td>
<td>3207</td>
<td>1556</td>
<td>1694</td>
<td>-</td>
<td>1167</td>
<td>551</td>
<td>502</td>
</tr>
<tr>
<td>([\text{CuL}^2\text{OAc}]^{6/5}\text{H}_2\text{O} \ (22))</td>
<td>-</td>
<td>1567</td>
<td>-</td>
<td>1599</td>
<td>1161</td>
<td>560</td>
<td>505</td>
</tr>
<tr>
<td>([\text{CuL}^2\text{N}_3\cdot\text{CH}_3\text{OH} \ (23))</td>
<td>-</td>
<td>1562</td>
<td>-</td>
<td>1586</td>
<td>1160</td>
<td>555</td>
<td>509</td>
</tr>
</tbody>
</table>

\(^a\) Newly formed C=N
Figure 5.2. IR spectrum of the compound \([\text{Cu}_3\text{L}_2\text{Cl}_4\text{]}\cdot4\text{H}_2\text{O}\) (15).

Figure 5.3. IR spectrum of the compound \([\text{CuL}_1\text{OAc}]\) (16).
Figure 5.4. IR spectrum of the compound $[\text{CuL}^1\text{NO}_3]_2$ (17).

Figure 5.5. IR spectrum of the compound $[\text{CuL}^1\text{N}_3]$ (18).
Cu(II) complexes of N₄-substituted semicarbazones: synthesis and spectral studies

Figure 5.6. IR spectrum of the compound [CuL¹SCN]⁻³/₂H₂O (19).

Figure 5.7. IR spectrum of the compound [Cu(HL¹)L¹]₂(ClO₄)₂·6H₂O (20).
The presence of a band in the spectrum of the semicarbazone, HL\textsuperscript{2} at 1702 cm\textsuperscript{-1} is due to $\nu$(C=O), which is shifted to 1694 cm\textsuperscript{-1} in the chloro complex \textbf{21}. This indicates that in this complex semicarbazone, HL\textsuperscript{2} is coordinated in the neutral, keto form. But this band is absent in complexes \textbf{22} and \textbf{23}, which means that in these complexes HL\textsuperscript{2} is coordinated as enol form. This is supported by the fact that in complexes \textbf{22} and \textbf{23} new bands are observed at 1599 and 1586 cm\textsuperscript{-1}, which are due to newly formed $\nu$(C=N) after enolization. However this band is absent in complex \textbf{21}. Upon complexation, the azomethine stretching vibration was shifted from 1592 cm\textsuperscript{-1} to lower wavenumbers in the range 1556-1567 cm\textsuperscript{-1}. In the complexes \textbf{21-23}, there is an increase in $\nu$(N–N) in the range 1160-1167 cm\textsuperscript{-1} which confirms the coordination of the semicarbazone through azomethine nitrogen.

For the chloro complex \textbf{21}, the bands at 1243 and 1119 cm\textsuperscript{-1} correspond to the in-plane vibrations of the quinoline ring while out-of-plane vibrations are observed at 744 and 686 cm\textsuperscript{-1}. The bands at 551 and 502 cm\textsuperscript{-1} are assigned to $\nu$(Cu–N\textsubscript{azo}) and $\nu$(Cu–O) respectively. For the acetato complex \textbf{22}, the band at 1249 cm\textsuperscript{-1} corresponds to the in-plane vibration of the quinoline ring while out-of-plane vibrations are observed at 753 and 692 cm\textsuperscript{-1}. The bands at 560 and 505 cm\textsuperscript{-1} are assigned to $\nu$(Cu–N\textsubscript{azo}) and $\nu$(Cu–O) respectively. For this complex, the bands at 1510 and 1469 cm\textsuperscript{-1} correspond to asymmetric and symmetric stretching vibrations of the acetate group respectively. For the azido complex \textbf{23}, a sharp band at 2054 cm\textsuperscript{-1} correspond to the asymmetric $\nu$(N\textsubscript{3}) mode. The band associated with the symmetric $\nu$(N\textsubscript{3}) mode is observed at 1344 cm\textsuperscript{-1}. The broad band observed at 652 cm\textsuperscript{-1} is assigned to $\bar{\nu}$(N–N–N). The bands at 1247 and 1118 cm\textsuperscript{-1} correspond to the in-plane vibrations of the quinoline ring while out-of-plane vibrations are observed at 751 and 692 cm\textsuperscript{-1}. The bands at 555 and 509 cm\textsuperscript{-1} are assigned to $\nu$(Cu–N\textsubscript{azo}) and $\nu$(Cu–O) respectively. The IR spectra of the complexes are presented in Figures 5.8-5.10.
Figure 5.8. IR spectrum of the compound $[\text{Cu(HL}_2\text{)}\text{Cl}_2]_2\cdot\text{H}_2\text{O}$ (21).

Figure 5.9. IR spectrum of the compound $[\text{CuL}_2\text{OAc}]^{6/3}\text{H}_2\text{O}$ (22).
5.3.2. Electronic spectra

The electronic spectral data of semicarbazones and copper(II) complexes recorded in DMSO solution are given in Table 5.3 and electronic spectra are shown in the Figures 5.11-5.17. The semicarbazones HL$^1$ and HL$^2$ have absorptions at 36300 and 36940 cm$^{-1}$ respectively due to $\pi-\pi^*$ transitions of the pyridyl ring/quinoline ring and imine function of the semicarbazone moiety. Bands in the region 28770-32200 cm$^{-1}$ correspond to $n-\pi^*$ transitions of the amide function [27] for HL$^1$ and HL$^2$. This intraligand transitions are observed in the range 32290-28800 cm$^{-1}$, which undergoes shift upon complexation. This shift may be due to the weakening of C=O bond and donation of lone pair of electrons to the metal on complexation.

The high intense ligand-to-metal charge transfer (LMCT) transitions are observed at high energy region. The intensity of these transitions reflects the overlap of the ligand and metal orbitals involved in the charge transfer. In all
the complexes 15-23, LMCT transitions are observed in the region 22100-24050 cm\(^{-1}\) and which are assigned to O→Cu and N→Cu LMCT transitions.

In the chloro complex 21 shoulder region is observed at 28800 cm\(^{-1}\), which is assigned as Cl→Cu charge-transfer transition [28]. For a tetragonal field three spin allowed transitions, \(^2\)A\(_{1g}\)→\(^2\)B\(_{1g}\), \(^2\)B\(_{2g}\)→\(^2\)B\(_{1g}\) and \(^2\)E\(_{g}\)→\(^2\)B\(_{1g}\) are possible and square pyramidal complexes have the \(d\_yz\), \(d\_xz\)→\(d\_x\_2\_y\_2\) and \(d\_z^2\)→\(d\_x\_2\_y\_2\) transitions. But it is difficult to resolve them into separate bands due to the very low energy difference between these bands. All copper(II) complexes 15-23 have very broad \(d\_d\) combination bands (Figures 5.18-5.21) in the range 14000-16000 cm\(^{-1}\) [29,30].

**Table 5.3.** Electronic spectral assignments of semicarbazones and their Cu(II) complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorbance, (\lambda_\text{max} \text{ (cm}^{-1})</th>
<th>LMCT</th>
<th>(d_d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL(^1)</td>
<td>36300, 31160</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[Cu(_3_L,_2_Cl,_4)\cdot4H(_2_O) (15)]</td>
<td>32030</td>
<td>23820</td>
<td>14590</td>
</tr>
<tr>
<td>[CuL(^1)OAc] (16)</td>
<td>31940</td>
<td>23880</td>
<td>15200</td>
</tr>
<tr>
<td>[CuL(^1)NO(_3)]_2 (17)</td>
<td>31780</td>
<td>24050</td>
<td>14590</td>
</tr>
<tr>
<td>[CuL(^1)N(_3)] (18)</td>
<td>32110</td>
<td>23940</td>
<td>16000</td>
</tr>
<tr>
<td>[CuL(^1)SCN]_3_H(_2_O) (19)</td>
<td>32290</td>
<td>23970</td>
<td>14600</td>
</tr>
<tr>
<td>[Cu(HL(_1)L(_1)]_2(ClO(_4)]_2\cdot6H(_2_O) (20)</td>
<td>31270</td>
<td>23630</td>
<td>15300</td>
</tr>
<tr>
<td>HL(^2)</td>
<td>36940, 32200, 31300, 29900, 28770</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[Cu(HL(_2)_Cl(_2)_2\cdotH(_2_O) (21)</td>
<td>31940, 30160</td>
<td>22100, 28800</td>
<td>15380</td>
</tr>
<tr>
<td>[CuL(^2)OAc]_5_H(_2_O) (22)</td>
<td>31780</td>
<td>22780</td>
<td>15620</td>
</tr>
<tr>
<td>[CuL(^2)N(_3)]_2\cdotCH(_3_OH) (23)</td>
<td>31860</td>
<td>22270</td>
<td>14000</td>
</tr>
</tbody>
</table>
Figure 5.11. Electronic spectrum of the compound $[\text{Cu}_3\text{L}_2\text{Cl}_4] \cdot 4\text{H}_2\text{O}$ (15).

Figure 5.12. Electronic spectrum of the compound $[\text{CuL}_1\text{OAc}]$ (16).
Figure 5.13. Electronic spectrum of the compound $[\text{CuL}_1 \text{NO}_3]_2$ (17).

Figure 5.14. Electronic spectrum of the compound $[\text{CuL}_1 \text{N}_3]$ (18).
Figure 5.15. Electronic spectrum of the compound $[\text{CuL}^1\text{SCN}]^{3/2}\text{H}_2\text{O}$ (19).

Figure 5.16. Electronic spectrum of the compound $[\text{Cu}(\text{HL}^2)\text{Cl}_2]_2\cdot\text{H}_2\text{O}$ (21).
Figure 5.17. Electronic spectrum of the compound $[\text{CuL}_2\text{N}_3]\cdot\text{CH}_3\text{OH}$ (23).

Figure 5.18. Electronic spectrum of the compound $[\text{Cu}_3\text{L}_2\text{Cl}_4]\cdot4\text{H}_2\text{O}$ (15) in the visible region.
Figure 5.19. Electronic spectrum of the compound \([\text{CuL}^1\text{N}_3\text{]}\) (18) in the visible region.

Figure 5.20. Electronic spectrum of the compound \([\text{CuL}^1\text{SCN}]^{3/2}\text{H}_2\text{O}\) (19) in the visible region.
5.3.3. Electron paramagnetic resonance spectra

EPR spectroscopy is a powerful tool to infer details about the structure of complexes formed by paramagnetic metal ions. It is the electronic analog of NMR spectroscopy that probes the nuclear spin of molecules. An easy application of EPR spectroscopy uses the Cu(II) ion, a particularly favorable example of a metal ion that exhibits a wide range of stereochemistry with a variety of intermediate situations. For coordination geometries corresponding to an elongated octahedron, a square pyramid or square planar, the ground state is $d_{x^2-y^2}$. When the coordination around Cu(II) ion is a compressed octahedron or a trigonal bipyramid, the ground state is $d_z^2$. EPR spectroscopy can distinguish the ground states $d_{x^2-y^2}$ and $d_z^2$ on the basis of the principal values of the $g$ tensor in the anisotropic spectra. The value of $g$ is the primary
empirical parameter that characterizes the response of a paramagnetic molecule and provides a quantitative measure of the molecule’s magnetic moment and is sensitive to the changes in the molecule’s electronic structure. The Cu(II) ion has an effective spin of $S=3/2$ and is associated with a spin angular momentum $m_s=\pm 1/2$, leading to a doubly degenerate spin state in the absence of magnetic field. In a magnetic field the degeneracy is lifted between these states and the energy difference between them is given by $E = h\nu = g\beta B$, where $h$ is the Planck’s constant, $\nu$ is the frequency, $g$ is the Lande’s splitting factor equals to 2.0023 (for a free electron), $\beta$ is the Bohr magneton and $B$ is the magnetic field.

The EPR spectra of polycrystalline sample at 298 K and solution at 77 K were recorded in the X-band with 100 kHz field modulation and $g$ factors were quoted relative to the standard marker TCNE ($g=2.00277$). The EPR spectra of the complexes recorded in polycrystalline state at room temperature provide information about the coordination environment around Cu(II) in these complexes. All these values are in good agreement with earlier reported values of semicarbazones [31].

The EPR spectra of the compounds 15, 17, 21 and 22 in the polycrystalline state at 298 K show only one broad signal at $g_{\text{iso}} = 2.089$, 2.129, 2.150 and 2.150 respectively (Figures 5.22-5.23). Such isotropic spectra arise from extensive exchange coupling through misalignment of the local molecular axes between different molecules in the unit cell (dipolar broadening) and enhanced spin lattice relaxation. This type of spectra unfortunately give no information about the electronic ground state of the Cu(II) ion present in the complex.
Figure 5.22. EPR spectrum of the compound \([\text{Cu}_3\text{L}_2\text{Cl}_4]\cdot4\text{H}_2\text{O} \ (15)\) in polycrystalline state at 298 K (Experimental (green) and simulated best fit (purple) of the EPR spectra).

Figure 5.23. EPR spectrum of the compound \([\text{CuL}_1\text{NO}_3]_2 \ (17)\) in polycrystalline state at 298 K (Experimental (green) and simulated best fit (purple) of the EPR spectra).
For the compounds 16, 18 and 20 we got axial spectra with well defined $g_{||}$ and $g_{\perp}$ features. The variation of $g_{||}$ and $g_{\perp}$ values in these complexes indicate the geometry of the compounds in the solid state is affected by the nature of the coordinating gegenions. The geometric parameter $G$ is calculated as $G = g_{||} - 2.0023/g_{\perp} - 2.0023$ for axial spectra and it is a measure of exchange interaction between copper centers in the polycrystalline compound. If $G > 4.4$, exchange interaction is negligible and if it is less than 4.4, considerable exchange interaction is indicated in the solid complex [32-34]. The geometric parameter $G$ for the compounds 16, 18 and 20, are 3.258, 2.448 and 2.441 respectively, which indicate the fact that the unit cells of the compounds contain magnetically equivalent sites. For the complexes 16, 18 and 20, $g_{||} > g_{\perp} > 2$ and $G$ values falling in the range 2–4 are consistent with a $d_{x^2-y^2}$ ground state.

![Figure 5.24. EPR spectrum of the compound [CuL\textsuperscript{1}OAc] (16) in polycrystalline state at 298 K (Experimental (green) and simulated best fit (purple) of the EPR spectra).](image)
Figure 5.25. EPR spectrum of the compound [CuL\textsubscript{1}N\textsubscript{3} \text{ (18)}] in polycrystalline state at 298 K (Experimental (green) and simulated best fit (purple) of the EPR spectra).

For the compound 19, we got three \( g \) values \( g_1 = 2.028 \), \( g_2 = 2.104 \) and \( g_3 = 2.306 \) which indicate rhombic distortion in geometry (Figure 5.26). In the spectra with \( g_3 > g_2 > g_1 \) rhombic spectral values, \( R = g_2 - g_1 / g_3 - g_2 \) may be significant. If \( R > 1 \), a predominant \( d_z^2 \) ground state is present and if \( R < 1 \) a predominant \( d_{x^2-r^2} \) state is present and if \( R = 1 \) then the ground state is approximately an equal mixture of \( d_z^2 \) and \( d_{x^2-r^2} \). For the complex 19, \( R < 1 \) suggesting a \( d_{x^2-r^2} \) ground state indicates that the exchange interaction is negligible. The EPR spectrum of the compound [CuL\textsubscript{2}N\textsubscript{3} \cdot CH\textsubscript{3}OH (23) is reverse axial (Figure 5.27) with well defined \( g_\parallel \) and \( g_\perp \) features. This axially
compressed spectra has $g_\perp > g_\parallel$ with 2.045 and 2.130 as $g_\parallel$ and $g_\perp$ values respectively. As $g_\perp > g_\parallel$ the ground state is $d_{z^2}$. Absence of half field signals for compounds reinforce the assumption of superexchange interactions.

Figure 5.26. EPR spectrum of the compound [CuL\textsuperscript{1}SCN]\textsuperscript{3/2}H\textsubscript{2}O (19) in polycrystalline state at 298 K.
Figure 5.27. EPR spectrum of the compound [CuL^2N_3]^+·CH_3OH (23) polycrystalline state at 298 K.

The solution spectra of all complexes were recorded in DMF at 77 K. An axial spectrum was obtained for compound 15 (Figure 5.28) with 2.250, 2.061 and 178.33 x 10^-4 cm^-1 as g_∥, g_⊥ and A_∥ values. In the low field region, seven hyperfine lines are obtained that are moderately resolved suggesting a dimeric structure with two copper centers. This seven line hyperfine splitting is due to interaction of the electrons with two copper nuclei (^{65,63}Cu, I = 3/2), so that electrons are exchanged between two Cu(II)
ions *via* the bridging chlorine atoms at a rate faster than EPR time scale. The binuclear nature was confirmed by the presence of half field signal ($\Delta M_s = \pm 2$) at ca. 1570 G with $g$ value 4.133. It is observed that $g$ values of this complex in the solid state at 298 K and in DMF at 77 K are not much different from each other hence the geometry around the Cu(II) ion is unaffected on cooling the solution to liquid nitrogen temperature. As $g_{||} > g_{\perp}$, the possibility of trigonal bipyramidal geometry has been ruled out and square pyramidal structure is suggested. Thus the coordination polyhedron comprises of one pyridyl nitrogen, azomethine nitrogen, enolate oxygen and chlorine atom and the bridging chlorine atom occupies the axial position.

![EPR spectrum of the compound [Cu$_3$L$_2$Cl$_4$]·4H$_2$O (15) in DMF at 77 K](image)

**Figure 5.28.** EPR spectrum of the compound [Cu$_3$L$_2$Cl$_4$]·4H$_2$O (15) in DMF at 77 K (Experimental (green) and simulated best fit (purple) of the EPR spectra).
In the compound 16, an axial spectrum is obtained with $g_\parallel$ 2.250 and $g_\perp$ 2.045 values. Spectrum of this complex (Figure 5.29) has four copper hyperfine lines in both parallel and perpendicular regions. $A_\parallel$(Cu) and $A_\perp$(Cu) are calculated to be $150 \times 10^{-4}$ and $16 \times 10^{-4}$ cm$^{-1}$ respectively. $A_{av}$ is calculated by using the formula $A_{av} = \frac{1}{3}(A_\parallel + 2A_\perp)$ and it is $60 \times 10^{-4}$ cm$^{-1}$.

Figure 5.29. EPR spectrum of the compound [CuL1OAc] (16) in DMF at 77 K (Experimental (green) and simulated best fit (purple) of the EPR spectra).

For the nitrato complex 17, in the parallel region three of the copper hyperfine lines are moderately resolved (Figure 5.30) while perpendicular features overlap the fourth one. Appearance of seven lines in the perpendicular region is due to nitrogen superhyperfine splitting. Here the $g_\parallel = 2.240$, $g_\perp = 2.051$ and $A_\parallel = 159 \times 10^{-4}$ cm$^{-1}$. The presence of half field signal indicates a dimeric structure for this complex ($g = 4.332$).
Figure 5.30. EPR spectrum of the compound [CuL1NO3]2 (17) in DMF at 77 K (Experimental (green) and simulated best fit (purple) of the EPR spectra).

For the azido complex 18 also we got an axial spectrum (Figure 5.31) with $g_\parallel = 2.233$, $g_\perp = 2.047$ and $A_\parallel = 152 \times 10^{-4}$ cm$^{-1}$ values. The spectrum shows well resolved four hyperfine lines in the parallel region corresponding to monomeric Cu(II) complex.

Figure 5.31. EPR spectrum of the compound [CuL1N$_3$ ] (18) in DMF at 77 K (Experimental (green) and simulated best fit (purple) of the EPR spectra).
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In thiocyanato complex 19, an axial spectrum (Figure 5.32) is obtained with four hyperfine lines having $g_{||} = 2.223$, $g_\perp = 2.066$ and $A_{||} = 195 \times 10^{-4} \text{ cm}^{-1}$ values.

![EPR spectrum of the compound $[\text{CuL}^1\text{SCN}]^{3/2}\text{H}_2\text{O}$ (19) in DMF at 77 K (Experimental (green) and simulated best fit (purple) of the EPR spectra).](image)

**Figure 5.32.** EPR spectrum of the compound $[\text{CuL}^1\text{SCN}]^{3/2}\text{H}_2\text{O}$ (19) in DMF at 77 K (Experimental (green) and simulated best fit (purple) of the EPR spectra).

In the EPR spectrum of five coordinate copper(II) complex $[\text{Cu(HL}^1\text{L}^1\text{)}_2\text{(ClO}_4\text{)}_2\text{H}_2\text{O}$ (20), the four hyperfine lines are observed in the parallel region and an axial spectrum is obtained with $g_{||} = 2.265$, $g_\perp = 2.077$ and $A_{||} = 150 \times 10^{-4} \text{ cm}^{-1}$ values. The EPR spectrum of the complex 21 is also axial. For compounds, 22 and 23 EPR spectra are also axial with four hyperfine lines characteristic of monomeric copper(II) complexes, which arise from coupling of the odd electron with Cu nuclei ($^{65}\text{Cu}$, $I = 3/2$). The $g_{||} > g_\perp$ values accounts to the distorted square based pyramid structure in five coordinated complexes 15 and 21 and rules out the possibility of a trigonal bipyramidal structure, which would be expected to have $g_{||} < g_\perp$. Here for the four coordinated complexes 16, 17, 18, 19, 22 and 23, $g_{||} > g_\perp$ which suggest a square planar geometry.
Table 5.4. EPR spectral assignments of Cu(II) complexes in polycrystalline state at 298 K and solution at 77 K

<table>
<thead>
<tr>
<th>Compound</th>
<th>Polycrystalline state (298 K)</th>
<th>DMF solution (77 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$g_{xx}$</td>
<td>$g_{yy}$</td>
</tr>
<tr>
<td>[Cu$_3$L$_2$Cl$_3$]Cl·4H$_2$O (15)</td>
<td>2.089</td>
<td>-</td>
</tr>
<tr>
<td>[CuL$^1$OAc] (16)</td>
<td>-</td>
<td>2.262</td>
</tr>
<tr>
<td>[Cu$_3$NO$_3$]$_2$ (17)</td>
<td>2.129</td>
<td>-</td>
</tr>
<tr>
<td>[Cu$_3$N$_3$] (18)</td>
<td>-</td>
<td>2.315</td>
</tr>
<tr>
<td>[CuL$^1$SCN]$^3/2$H$_2$O (19)</td>
<td>-</td>
<td>2.306</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cu(L$^1$)Cl$_2$]Cl·6H$_2$O (20)</td>
<td>-</td>
<td>2.297</td>
</tr>
<tr>
<td>[Cu(L$^2$)Cl$_2$]Cl·H$_2$O (21)</td>
<td>2.150</td>
<td>-</td>
</tr>
<tr>
<td>[CuL$^2$OAc]$^3/2$H$_2$O (22)</td>
<td>2.150</td>
<td>-</td>
</tr>
<tr>
<td>[Cu$_2$N$_3$]CH$_3$OH (23)</td>
<td>-</td>
<td>2.045</td>
</tr>
</tbody>
</table>

$^a$A values in $10^3$ cm$^{-1}$
For the six coordinated compound 20 as the $g_{\|} > g_{\perp}$ distorted octahedral geometry is suggested. For all the compounds $g_{av}$ is also calculated using the equation, $g_{av} = 1/3 (g_{\|}+2g_{\perp})$ and it is in the range 2.109 - 2.232. According to Kivelson and Neiman considerable covalent character is suggested for M–L bond for the complexes when the $g_{\|} < 2.3$ [35]. The $g_{\|}$ values in all these complexes are less than 2.3 is an indication of covalent bonding in these complexes. The $g_{\|}$ values are nearly the same for all the complexes indicating that the bonding is dominated by the semicarbazone moiety. The EPR spectral assignments are given in Table 5.4.

The EPR bonding parameters are given in Table 5.5. The EPR parameters $g_{\|}$, $g_{\perp}$, $A_{d}(Cu)$ and the energies of $d$-$d$ transitions were used to evaluate the bonding parameters $\alpha^2$, $\beta^2$ and $\gamma^2$ which may be regarded as measures of covalency of the in-plane $\sigma$ bonds, in-plane $\pi$-bonds and out-of-plane $\pi$-bonds respectively. The value of in-plane $\sigma$-bonding parameter $\alpha^2$ was estimated from the expression,

$$\alpha^2 = -A_{d}/0.036 + (g_{\|} - 2.00277) + 3/7 (g_{\perp} - 2.00277) + 0.04$$ [36,37]

The orbital reduction factors, $K_{\|}^2 = \alpha^2\beta^2$ and $K_{\perp}^2 = \alpha^2\gamma^2$ were calculated using the following expressions [38].

$$K_{\|}^2 = (g_{\|} - 2.00277) E_{d-d}/8\lambda_0$$
$$K_{\perp}^2 = (g_{\perp} - 2.00277) E_{d-d}/2\lambda_0$$

Where $\lambda_0$ is the spin orbit coupling constant with a value of -828 cm$^{-1}$ for Cu(II) d$^9$ system.

According to Hathaway [34], for pure $\sigma$ bonding $K_{\|} \approx K_{\perp} \approx 0.77$, and for in-plane $\pi$-bonding, $K_{\|} < K_{\perp}$; while for out-of-plane $\pi$-bonding, $K_{\perp} < K_{\|}$. In
the complexes, except 19, 20, 21 and 22, it is observed that $K_\perp < K_{||}$ which indicates the presence of significant out-of-plane $\pi$-bonding. In the complexes 19, 20, 21 and 22, $K_{||} < K_\perp$ indicate in-plane $\pi$-bonding. Furthermore, $\alpha^2$, $\beta^2$ and $\gamma^2$ have values less than 1 which is expected for 100% ionic character of bonds; suggest the covalency of the bonds. But in complex 21, the value of $\gamma^2$ is unexpected and is greater than 1. The empirical factor $f = g_{||} / A_{||} (\text{cm}^{-1})$ is an index of tetragonal distortion and depends on the nature of the coordinated atom. In all the compounds, $f$ falls in the range 114-151 cm$^{-1}$ corresponding to a Cu(II) center with medium to extreme distortion [39].

### Table 5.5. EPR bonding parameters of Cu(II) complexes

| Compound                                      | $\alpha^2$ | $\beta^2$ | $\gamma^2$ | $K_\perp$ | $K_{||}$ | $K_{\perp}$ | $f^a$ |
|-----------------------------------------------|------------|-----------|------------|-----------|----------|------------|------|
| [Cu$_3$L$_2^1$Cl$_4$]·4H$_2$O (15)            | 0.807      | 0.674     | 0.635      | -         | 0.738    | 0.716      | 126.17|
| [Cu$L^1$OAc] (16)                            | 0.721      | 0.785     | 0.536      | -         | 0.753    | 0.622      | 150.00|
| [Cu$L^1$NO$_3$]$_2$ (17)                      | 0.739      | 0.774     | 0.630      | -         | 0.756    | 0.682      | 140.88|
| [Cu$L^1$N$_3$] (18)                           | 0.711      | 0.718     | 0.551      | -         | 0.714    | 0.626      | 146.90|
| [Cu$L^1$SCN]$^{3/2}$H$_2$O (19)               | 0.829      | 0.614     | 0.704      | -         | 0.713    | 0.764      | 114.01|
| [Cu(HL$_1$)]$^1$L$_2$(ClO$_4$)$_2$·6H$_2$O (20)| 0.750      | 0.806     | 0.913      | -         | 0.778    | 0.828      | 151.00|
| [Cu(HL$_2$)$_2$Cl$_2$·2$H_2$O (21)            | 0.794      | 0.671     | 2.078      | -         | 0.730    | 1.288      | 149.78|
| [Cu$L^2$OAc]$^{4/5}$ H$_2$O (22)              | 0.788      | 0.646     | 0.911      | -         | 0.714    | 0.847      | 122.15|
| [Cu$L^2$N$_3$]CH$_3$OH (23)                   | 0.723      | 0.793     | 0.649      | -         | 0.757    | 0.685      | 149.53|

*a Expressed in units of cm.
References


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